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LOW-MELTING LOW-LEAD GLASSES BASED ON BORATE SYSTEMS

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The results of experimental studies of the production of low-melting glasses with low lead oxide content for fluxes of silicate paints based on two borate systems not previously studied are presented. The predictable changes of the softening onset temperature, the total flow, and the CLTE are established. The crystallization power of the glasses is studied. The results of these investigations are used as a basis to propose compositions with 20 – 25 wt.% PbO (molar content 6 – 10%) and burn-in temperature of paints based on them 560 – 580°C.

Key words: low-melting glasses, borate systems, fluxes, silicate paints.

Interest in low-melting glasses has increased considerably in the recent years. Such paint is needed not only in the technologies for decorating and marking glass articles but also in opto-electronic technology. For this reason, the range of compositions of the proposed glasses is expanding substantially in the direction of lower content of toxic lead oxide and introduction of new oxides which impart specific properties to low-melting glasses [1]. But even when new oxides are used it is not always possible to decrease the amount of PbO introduced.

In addition to the previously published data [1], the compositions of low-melting glasses according to patent sources are indicated. Examples are compositions of low-melting glasses for the connections of the components of magnetic heads. In RF patent No. 1319487 the following composition is proposed for the glass (%[2]): 54.0 – 64.0 PbO, 10.4 – 11.0 B_2O_3, 2.6 – 3.0 SiO_2, 0.1 – 1.0 Al_2O_3, 15.0 – 22.0 Bi_2O_3, 5.7 – 6.0 ZnO, 0.2 – 4.5 Y_2O_3. The glassmaking temperature is 1100°C. In RF patent No. 2016863 the glass composition is (%): 31.90 – 34.19 PbO, 3.50 – 4.00 ZnO, 3.48 – 3.97 BaO, 0.01 – 0.39 P_2O_5, 4.97 – 8.41 Bi_2O_3, 5.87 – 6.60 Nb_2O_5, 0.01 – 0.58 Ta_2O_5, 0.41 – 0.67 F^-, 3.01 – 3.92 MoO_3, 2.60 – 3.00 Sb_2O_5, 0.01 – 0.22 B_2O_3, 0.01 – 2.91 Al_2O_3. Its flow temperature is below 400°C.

A low-melting glass with the following composition (%) containing lead in the form PbF_2 is (RF patent No. 1533244): 29.27 – 58.01 PbF_2, 15.65 – 19.30 B_2O_3, 0.20 – 1.00 ZnO, 0.10 – 1.50 CdO, 23.18 – 53.38 Bi_2O_3, 0.05 – 4.13 Al_2O_3, 0.01 – 1.50 CuO, 0.01 – 0.50 NiO. The softening onset temperature is 290 – 385°C, the deformation onset temperature is 330 – 358°C, and the flow temperature is 500°C.

Compositions of lead-free or low-lead glasses but with a substantial content of V_2O_5 have also been proposed (RF patent No. 2044710) for the same purposes (%): 38.60 – 48.90 B_2O_3, 9.13 – 14.70 ZnO, 0.10 – 2.60 Li_2O, 7.80 – 16.30 Na_2O, 27.40 – 39.60 V_2O_5, 0.10 – 3.00 Al_2O_3, 0.50 – 4.00 BaO. The flow temperature is less than 580°C, and the CLTE is $(93 - 135) \times 10^{-7}\ K^{-1}$. In addition, glasses with the following compositions (RF patent No. 1736107) have been proposed (%): 4.50 – 11.00 PbO, 0.01 – 0.90 ZnO, 0.01 – 1.00 BaO, 16.00 – 20.00 Đ$_2$Î$_5$, 0.01 – 2.50 Bi_2O_3, 0.001 – 1.00 CuO, 0.01 – 1.10 B_2O_3, 13.00 – 25.00 Sb_2O_3, 49.00 – 60.00 V_2O_5.

Glass with the following composition is proposed in RF patent No. 2015121 (%): 21.0 – 23.0 ZnO, 15.0 – 18.0 CdO, 16.0 – 18.0 B_2O_3, 14.0 – 15.0 PbF_2, 13.0 – 16.0 PbO, 10.0 – 12.0 SnO_2, 4.0 – 5.0 Ga_2O_3. The softening temperature is 310 – 315°C, and the glassmaking temperature is 800 ± 50°C. But the introduction of considerable amounts of PbO, and in part PbF_2, does not solve the problem of developing low-lead glass compositions.

A number of new low-melting glasses still have a high content of PbO.

Compositions for low-melting glasses to be used in soldering and sealing are presented. In RF patent No. 2152909 the glass composition is (%): 80.5 – 82.5 PbO, 5.5 – 7.5 B_2O_3, 1.0 – 2.5 Bi_2O_3, 5.5 – 6.5 ZnO, 0.5 – 0.9 SiO_2, 1.5 – 3.5 Co_2O_3, 1.0 – 1.5 Cu_2O. The glass is not only low-lead but it contains coloring oxides, which preclude its use as a flux for silicate paints.

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[2] Here and below, unless otherwise stated, the content by weight.

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TABLE 1.

Glass	Composition of the experimental glasses							
	content, wt.%*			molar content, %				
	B_2O_3	ZnO	PbO	B_2O_3	ZnO	PbO	CaO	Li_2O
1	40	25	20	43.6	23.3	6.8	13.6	12.7
2	35	30	20	38.5	28.5	6.9	13.7	12.8
3	30	35	20	33.2	33.2	6.9	13.8	12.9
4	25	40	20	27.9	38.2	6.9	13.9	13.0
5	20	45	20	22.5	43.3	7.1	14.0	13.1
6	35	25	25	39.7	24.2	8.8	14.1	13.1
7	30	30	25	34.3	29.3	8.9	14.2	13.3
8	25	35	25	28.8	34.5	9.0	14.3	13.4
9	20	40	25	23.2	39.7	9.1	14.5	13.5
10	30	25	30	35.4	25.2	11.0	14.7	13.7
11	35	30	30	29.7	30.5	11.1	14.8	13.8
12	20	35	30	24.0	35.9	11.2	14.9	14.0
13	25	25	35	30.7	26.3	13.4	15.3	14.3
14	20	30	35	24.8	31.8	13.5	15.4	14.4
15	25	25	40	25.6	27.4	16.0	16.0	14.9
16	45	20	20	48.7	18.5	6.8	13.5	12.5
17	40	20	25	44.2	19.5	8.9	14.2	13.2
18	35	20	30	40.9	20.0	10.9	14.6	13.6
19	30	20	35	36.5	20.8	13.3	15.2	14.2
20	25	20	40	31.8	21.8	15.8	15.8	14.8

* All compositions contained 10% CaO and 5% Li_2O.

The following glass composition is proposed in USSR Inventor's Certificate No. 1567536 (%): 16.0 – 33.0 PbO, 2.0 – 2.5 B_2O_3, 1.0 – 1.5 SiO_2, 3.0 – 6.0 ZnO, 60.0 – 75.0 Bi_2O_3. However, the CLTE of this glass is (120 – 135) × 10^{-7} K^{-1}, which does not meet the requirement for fluxes for silicate paints. The following glass composition is proposed in RF patent No. 2237623 for the same purposes (%): 4.8 – 47.0 Bi_2O_3, 33.8 – 59.3 PbO, 8.3 – 12.3 ZnO, 2.0 – 2.5 SiO_2, 5.6 – 6.8 B_2O_3. The glassmaking temperature is 850 – 900°C.

Finally, a number of compositions of low-melting glasses have been developed for decoration and marking glass articles. The following compositions are proposed (%): RF patent No. 2325336 — 50.0 – 10.0 SiO_2, 3.0 – 5.0 Al_2O_3, 3.0 – 5.0 B_2O_3, 63.0 – 66.0 PbO, 1.8 – 2.8 CdO, 15.0 – 20.0 CaO, 0.1 – 0.2 S^{2-}; RF patent No. 2326072 — 73.0 – 77.0 PbO, 10.0 – 15.0 B_2O_3, 3.5 – 5.0 SiO_2, 1.0 – 1.5 Nd_2O_3, 6.0 – 8.0 MgO; RF patent No. 2328459 — 18.0 – 24.0 PbO, 4.0 – 8.0 SiO_2, 12.0 – 18.0 Al_2O_3, 2.0 – 4.0 BaO, 37.0 – 45.0 CaO, 1.0 – 2.0 MgO, 6.0 – 10.0 Li_2O, 1.0 – 2.0 dye; RF patent No. 2326826 — 60.0 – 65.0 PbO, 3.0 – 5.0 SiO_2, 5.0 – 7.0 B_2O_3, 3.0 – 5.0 ZnO, 22.0 – 25.0 CaO.

All these compositions not only contain a large quantity of PbO but they are also distinguished by high reactivity with respect to priming charges with high CaO content, which sharply increases the CLTE.

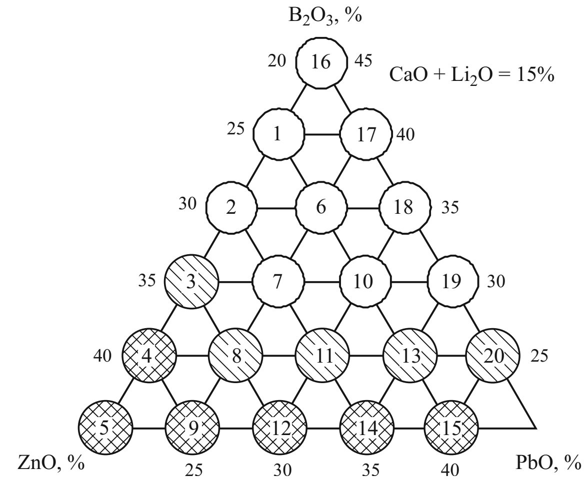

Fig. 1. Results of making the experimental glasses:) transparent glasses;) partially opacified glasses;) crystallization during production.

Practically the only lead-free glass is one proposed in RF patent No. 2070868 (%): 35.0 – 39.0 SiO_2, 24.0 – 28.0 B_2O_3, 0.5 – 2.0 ZnO, 0.5 – 3.0 CaO, 8.0 – 12.0 Na_2O, 4.5 – 10.0 K_2O, 1.5 – 4.0 Li_2O, 1.0 – 5.0 P_2O_5, 1.0 – 3.0 Al_2O_3, 10.0 – 14.0 TiO_2. The flow temperature is 560 – 610°C. The main advantage of this glass is that it contains no PbO. However, the substantial content of alkali oxides lowers the chemical stability and increases the CLTE considerably.

Thus the development of low-melting glasses for fluxes used for preparing paints with low PbO content, no expensive components, and CLTE (80 – 90) × 10^{-7} K^{-1}, for decorating and marking glass articles remains a topical problem.

This article presents the results of experimental studies, performed on the basis of borate systems, on obtaining low-lead fluxes.

The system Li_2O – CaO – PbO – ZnO – B_2O_3 with constant content 10% CaO and 5% Li_2O, not previously studied, was chosen on the basis of an analysis of published data and the results of previous work, performed at the Belarus State Technological University, on synthesizing low-melting fluxed. The initial materials were H_3BO_3, Pb_3O_4, ZnO, $CaCO_3$, and Li_2CO_3.

The compositions of the glasses synthesized are presented in Table 1. It is characteristic that with respect to the molar content the amount of CaO and Li_2O in the glasses varies very little, while the molar content of PbO ranges from 6.8 to 16%. Borate glasses with such a low molar content of PbO have not been studied previously. A fifth-order Scheffé plan was used to plan the glass compositions.

The glasses were made in 0.2 liter porcelain crucibles an electric furnace with maximum temperature 900 – 1000°C. The results are presented in Fig. 1.

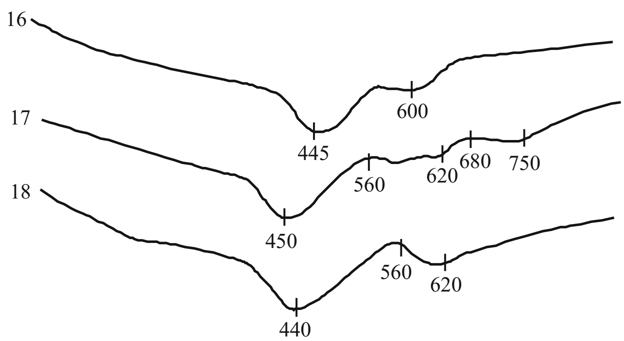

Fig. 2. DTA curves (°C) for the glasses 16, 17, and 18 which show no tendency toward crystallization during gradient heat-treatment.

Glasses with 30 – 45% B_2O_3 form well, are well fined, and remain transparent on extraction. Glasses with higher B_2O_3 content partially crystallize on extraction, though the initial melts are transparent. The effect of PbO on the stability of the glassy state in the experimental system is negligible.

All glasses which did not crystallize on extraction were heat-treated in a gradient furnace at temperatures 400 – 800°C for 1 h. It was of interest to determine the proneness of the glasses to crystallization during heat-treatment.

It was determined that all glasses obtained show a quite weak tendency to crystallize during gradient heat-treatment. Only the appearance of a weakly expressed crystalline film is observed in glasses containing 25 and 30% ZnO. For glasses 6, 17, and 18 absolutely no indications of crystallization were observed. When the soaking time at 400 – 800°C is increased to 3 h a thin crystalline crust appears on glasses 16, 17, and 18.

The DTA curves of these glasses show two endothermal effects (Fig. 2), due to liquation phenomena, in the temperature intervals 440 – 450 and 600 – 620°C. Electron-microscopic studies confirm the presence of two glassy phases; the amount of the second (liquating) phase is negligible. The softening onset temperature $t_{s.o}$ (corresponding to the first endo-effect) is such that these glasses can serve as a basis for obtaining fluxes.

The x-ray diffraction pattern of the crystallized glass 18 is revealing (Fig. 3). In the first place, halos corresponding to two glassy phases are clearly visible (at $2\theta = 10 – 20$ and $22 – 34°$). In the second place, only the second phase, whose content is lower, crystallizes. According to the interplanar distances (0.2704, 0.2537, and 0.2263 nm) one crystalline phase belonging to the monoclinic system with composition $Li_2O \cdot 2ZnO \cdot B_2O_3$ separates. Evidently, the composition of the liquated phase is close to that of this compound.

Figure 4 shows $t_{s.o}$ and CLTE versus the composition in the experimental system. The very weak dependence $t_{s.o}$ on the composition of the glass in the range studied draws our attention. All values of $t_{s.o}$ fall into a narrow temperature interval from 410 to 450°C.

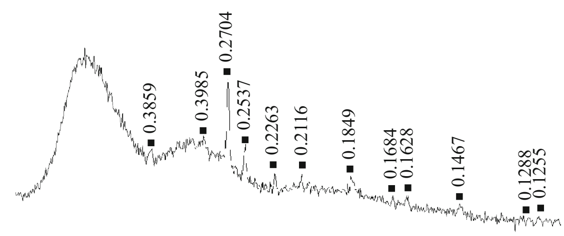

Fig. 3. X-ray diffraction pattern of the glass 18 (nm): ■) lithium-zinc borate $Li_2O \cdot 2ZnO \cdot B_2O_3$.

Analysis of the variation of $t_{s.o}$ as a function of the composition of the glasses leads to the conclusion that replacing ZnO with PbO with constant B_2O_3 content has no effect whatsoever on the value of $t_{s.o}$.

A sharp feature of the experimental glasses was revealed: the value of $t_{s.o}$ depends only on the B_2O_3 content (for the same total content of PbO and ZnO), i.e. replacing PbO with ZnO does greatly affect the value of $t_{s.o}$.

The structural role of PbO and ZnO can be expected to be practically identical in glasses in the borate system. The smooth dependence of $t_{s.o}$ on the B_2O_3 content for different PbO and ZnO ratios shows that neither ZnO nor PbO promotes coordination transitions of the boron ions. However, the unexpected increase of $t_{s.o}$ with increasing B_2O_3 content draws our attention; it could be due to an increase in the fraction of quadruply coordinated boron in the presence of CaO.

The value of CLTE determines the suitability of the flux for soldering with glass. The CLTE of top quality and packaging articles which are decorated with silicate paints is $(85 – 95) \times 10^{-7}\ K^{-1}$. The difference in the values of the CLTE of glass and flux with pigments should not exceed ± 10%.

The CLTE of the experimental glasses ranges from 70×10^{-7} to $90 \times 10^{-7}\ K^{-1}$. This gives a basis for concluding that these glasses can be used as fluxes. The glasses 17 and 18 with CLTE from 80×10^{-7} to $85 \times 10^{-7}\ K^{-1}$ are of greatest interest. Figure 4 shows lines of equal values for the CLTE in the range of the experimental glasses. The values of the CLTE are observed to increase somewhat with increasing PbO content and then decrease considerably with increasing B_2O_3 content.

All glasses show high resistance to water. The mass losses with boiling for 1 h do not exceed 1%.

Considering the high cost of the lithium-containing initial material, replacement of Li_2O with K_2O was studied, i.e., glasses in the system $K_2O – CaO – PbO – ZnO – B_2O_3$ were synthesized. The glasses were obtained at temperature 1100°C with soaking for 1 h. All glasses were made and fined well under such conditions.

A characteristic feature of these glasses is the complete absence of any indications of crystallization during treatment in a gradient furnace at temperature 400 – 900°C for 1 h. But a considerable difference in the deformation onset temperature (fusion of sharp faces) and complete spreading (zero-

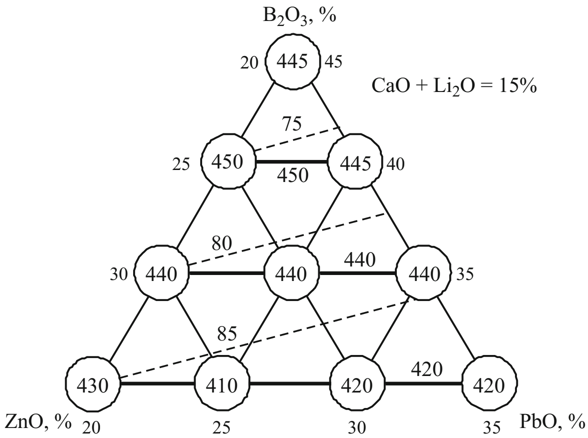

Fig. 4. Lines of equal values for $t_{s.o}$ and CLTE (10^{-7} K^{-1}) of the experimental glasses: solid lines — $t_{s.o}$; dashed lines — CLTE.

meniscus temperature) as compared with lithium glasses were observed. All corresponding temperatures for the potassium glasses were approximately 80 – 100°C higher. Thus, these temperatures fall into the following ranges t_{def} = 680 – 720°C, t_{sp} = 750 – 790°C for potassium glasses and t_{def} = 520 – 600°C, t_{sp} = 650 – 720°C for lithium glasses.

The softening onset temperature also increases. Evidently, this is due to the fact that the potassium cation with a large radius (0.133 versus 0.068 nm in lithium) promotes more active transition of a portion of the boron ions from triple to quadruple coordination. At the same time the degree of linkage of the structural network of borate glass increases and its thermal properties — $t_{s.o}$ and t_{sp} — improve. IR spectroscopy confirms that the fraction of triply coordinated boron decreases with a transition from lithium to potassium glasses — the intensity of the absorption bands at 1365 – 1370 and 1230 – 1235 cm^{-1}, which belong to [BO_3] groups, decreases and absorption in the region 1000 – 1040 cm^{-1}, due to [BO_4] groups, increases.

In summary, the glasses 16 and 17 in the lithium series are recommended as optimal. They were used as a basis for obtaining decorative coatings on articles made of high-quality glass with burn-in temperature 560 – 580°C. These coatings had good flowability at these temperatures and a high degree of adhesion to the high-quality glass.

REFERENCES

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